

SYNTHESES OF POLYHEDRANES AND POLYHEDRAL CARBORANES(U)  
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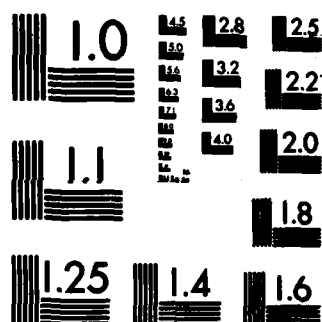
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**FINAL REPORT**

to the

**Army Research Office**

**Post Office Box 12211**

**Research Triangle Park**

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on

**SYNTHESES OF POLYHEDRANES AND POLYHEDRAL CARBORANES**

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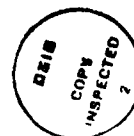
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## INTRODUCTION

Polyhedral cage molecules containing the light elements boron or carbon at each of the vertices of the polyhedron are of considerable current interest to the Army as intermediates for the preparation of materials for diverse applications ranging from high energy propellants and explosives to thermally stable polymers. The scientific goal of this research program was the discovery and development of fundamental chemistry relevant to the synthesis of polyhedral cage molecules of important to the Army.

The target molecules of this research project can be classified into the following two types:

(1) Polyhedral boranes of the type  $B_nH_n^{2-}$  and carboranes of the type  $C_2B_nH_{n+2}$  and their substitution products: Such compounds are based on polyhedra having exclusively triangular faces (deltahedra). These compounds, known as closo compounds, are extensively delocalized systems having  $2v + 2$  skeletal electrons where  $v$  is the number of vertices of the deltahedron, each BH vertex contributes two skeletal electrons, and each CH vertex contributes three skeletal electrons.<sup>1,2,3</sup> The neutral species  $C_2B_nH_{n+2}$  and their substitution products are of greater interest than the ionic species  $B_nH_n^{2-}$  since ionic species are necessarily accompanied by a counterion which might interfere with ultimate practical applications.

(2) Polyhedranes of the type  $(CH)_n$  and their substitution products where  $n$  in principle can be any even number other than 2: Such compounds are based on polyhedra in which three edges meet at each vertex. These systems exhibit localized chemical bonding in which each edge of the polyhedron corresponds to a normal two-electron two-center carbon-carbon

single bond. Tetrahedrane ( $n = 4$ ), cubane ( $n = 8$ ), dodecahedrane ( $n = 20$ ), and prismane ( $n = 6$ ) are the four most obvious of the many possible polyhedranes.<sup>4</sup>

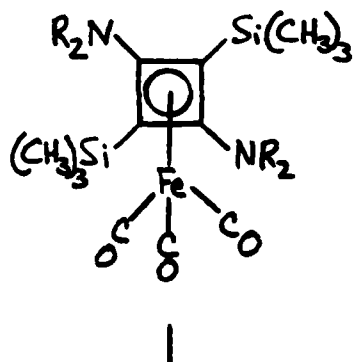
Both of these types of compounds are based on polyhedra having boron or carbon atoms at each vertex and one external monovalent group (hydrogen, alkyl, halogen, cyano, nitro, etc.) bonded to each of the vertex atoms.

The general synthetic approach investigated in this project was the coupling of polyhedral fragments to form the desired polyhedral cage molecule. In connection with the development of improved syntheses of polyhedral boranes and carboranes we sought more direct routes for the conversion of borohydride to these systems through intermediates such as borane adducts and the octahydrotriborate anion.<sup>5</sup> In connection with the synthetic of functionalized tetrahedranes and cubanes, we sought new approaches for the dimerization of functionalized alkynes.

The experiments in borane chemistry, discussed below in further detail, were uniformly unsuccessful although some observations on the reaction of  $B_3H_8^-$  with  $WCl_6$  suggested that interesting species might be obtainable from reactions of  $B_3H_8^-$  with early transition metal halide derivatives provided appropriate stabilizing ligands can be found. The experiments on the dimerization of functionalized alkynes led to the discovery of the head-to-tail 2+2 cyclodimerization of dialkylamino-trimethylsilylacetylenes,  $R_2NC\equiv Si(CH_3)_3$  ( $R_2N$  = diethylamino, piperidino, etc.) with iron carbonyls to give the corresponding cyclobutadiene complexes I. Unfortunately, conditions were not found for the degradation of the iron tricarbonyl complexes I to the corresponding free cyclobutadienes or compounds derived therefrom despite attempts using most of the oxidizing agents (e.g.,  $Ce^{IV}$ ,  $Fe^{III}$ , lead tetraacetate, trimethyl-



amine N-oxide, etc.) effective at liberating other cyclobutadienes from their iron tricarbonyl complexes.<sup>6</sup> A variety of attempts were also made to functionalize the tetralithiotetrahedrane of Schleyer and co-workers<sup>7</sup> using the halides  $(\text{CH}_3)_3\text{ECl}$  ( $\text{E} = \text{Si}$  or  $\text{Sn}$ ) in an attempt to obtain a tetrahedrane of the type  $[(\text{CH}_3)_3\text{E}]_4\text{C}_4$  analogous to the stable<sup>8,9</sup>  $[(\text{CH}_3)_3\text{C}]_4\text{C}_4$ . However, these were uniformly unsuccessful. In fact at the present time there seems to be a valid question as to whether the  $\text{Li}_4\text{C}_4$  reagent reported by Schleyer and co-workers is really tetralithiotetrahedrane as claimed by them in 1978.<sup>7</sup>



## NEW RESULTS FROM THIS RESEARCH PROGRAM

### (1) New Approaches to the Synthesis of Polyhedral Boranes and Carboranes

The general objective of our work on polyhedral borane synthesis was the development of new methods for converting the relatively inexpensive borohydride to polyhedral boranes, metallaboranes, and carboranes. Initially we attempted condensation reactions of the  $\text{BH}_3$  units in borane complexes using transition metal complexes. In this connection the following transition metal complexes were exposed to ultraviolet irradiation for 24 hr. in pentane solution in the presence of excess borane-tetrahydrofuran or borane-dimethyl sulfide:  $(\text{C}_5\text{H}_5)_2\text{Ni}$ ,  $[\text{C}_5\text{H}_5\text{NiCO}]_2$ ,  $(\text{C}_5\text{H}_5\text{Ni})_2\text{C}_2\text{R}_2$  ( $\text{R} = \text{H}$ ,  $\text{CH}_3$ , and  $\text{C}_2\text{H}_5$ ),  $\text{HCCo}_3(\text{CO})_9$ ,  $\text{R}_2\text{C}_2\text{Co}_2(\text{CO})_6$  ( $\text{R} = \text{H}$  and  $\text{C}_2\text{H}_5$ ),  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Mn}(\text{CO})_5\text{Br}$ . These complexes were selected in order to provide potential sources of  $\text{C}_5\text{H}_5\text{Ni}$ ,  $\text{Co}(\text{CO})_3$ , and  $\text{RC}$  vertices which are known building blocks for deltahedral metallo-carboranes.

In general these photochemical reactions gave dark suspensions. Solvent was removed from these reaction mixtures in vacuum. The residues were extracted with solvents such as pentane, dichloromethane, and acetone. Such extracts were concentrated to about 10 ml. and chromatographed on alumina. The chromatograms were eluted with pentane, dichloromethane, and finally acetone. The only observed organometallic compounds from such chromatograms were some unchanged organometallic starting material in a few cases.

The reactions of  $(\text{C}_5\text{H}_5)_2\text{Ni}$  and  $\text{Fe}_2(\text{CO})_9$  with borane-tetrahydrofuran were also investigated in boiling tetrahydrofuran in the absence of ultraviolet irradiation. A similar workup procedure as outlined above led to negative results in all cases.

These results suggest that photochemical reactions of transition metal complexes with  $\text{BH}_3$  derivatives are not promising for the synthesis of deltahedral carboranes. We therefore turned to an investigation of transition metal derivatives of the octahydrotriborate anion,  $\text{B}_3\text{H}_8^-$  which can be obtained readily in good yield<sup>5</sup> by iodination of tetrahydroborate according to the following equation:



Furthermore, at the start of this work the octahydrotriborate ligand was known to form a variety of metal carbonyl complexes<sup>10</sup> such as  $\text{B}_3\text{H}_8\text{Mn}(\text{CO})_4$ ,  $\text{HFe}(\text{CO})_3\text{B}_3\text{H}_8$ , and  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{B}_3\text{H}_8$ . From the point of view of the transition metal chemist the  $\text{B}_3\text{H}_8$  ligand may be regarded as a three-electron donor like the trihaptoallyl ligand. From the point of view of the boron hydride chemist these  $\text{B}_3\text{H}_8$  transition metal complexes can be regarded as analogues of tetraborane,  $\text{B}_4\text{H}_{10}$ , in which one of the boron vertices is replaced by a transition metal vertex. In this context the  $\text{B}_3\text{H}_8$  transition metal complexes can be viewed as relatively open boranes potentially susceptible towards reactions with alkynes to form six-vertex metallacarboranes. For example, a species of the composition  $\text{R}_2\text{C}_2\text{B}_3\text{H}_4\text{Mn}(\text{CO})_3$  potentially obtainable from  $\text{B}_3\text{H}_8\text{Mn}(\text{CO})_4$  and an appropriate alkyne would have the 14 skeletal electrons expected for a closo metallacarborane with a  $\text{C}_2\text{B}_3\text{Mn}$  octahedron.<sup>1</sup>

These considerations led to a study of the reactions of  $\text{B}_3\text{H}_8\text{Mn}(\text{CO})_4$  with various alkynes. At room temperature  $\text{B}_3\text{H}_8\text{Mn}(\text{CO})_4$  appeared to be unreactive towards even unsubstituted acetylene in dichloromethane solution. However, ultraviolet irradiation of  $\text{B}_3\text{H}_8\text{Mn}(\text{CO})_4$  with either unsubstituted acetylene or diethylacetylene resulted in reactions to give complex mixtures of manganese carbonyl derivatives in low yield. Since infrared and mass spectrometric studies of these manganese carbonyl

derivatives indicated the absence of borane ligands, they were not investigated in detail. These studies suggest that reactions of  $B_3H_8Mn(CO)_4$  with alkynes result in facile cleavage of the  $B_3H_8-Mn$  bond.

A metallaborane with interesting potential chemical reactivity is  $HFe(CO)_3B_3H_8$ , a volatile, thermally unstable yellow liquid readily prepared from  $Fe(CO)_4X_2$  ( $X = Br$  or  $I$ ) and  $R_4N^+B_3H_8^-$  (ref. 10). This iron carbonyl hydride can be viewed either as an analogue of  $B_4H_{10}$  or as an analogue of  $HMn(CO)_5$  or  $HCo(CO)_4$ . Furthermore, a particularly interesting chemical property of  $HFe(CO)_3B_3H_8$  is its thermal conversion to the known<sup>11</sup>  $B_4H_8Fe(CO)_3$  at room temperature. The yield of the reaction is low ( $\sim 3\%$ ), which is scarcely surprising since the conversion of an  $FeB_3$  system to an  $FeB_4$  system in the absence of additional boron hydride species must involve nearly total destruction of some of the  $HFe(CO)_3B_3H_8$  to generate the extra boron vertex. Since the conversion of  $HFe(CO)_3B_3H_8$  to  $B_4H_8Fe(CO)_3$  represents a further key step in the conversion of  $BH_4^-$  to higher boranes, this reaction was investigated. The yield of  $B_4H_8Fe(CO)_3$  from the decomposition of  $HFe(CO)_3B_3H_8$  at room temperature was found to be improved rather significantly from  $\sim 3\%$  to  $\sim 15\%$  if excess borane-tetrahydrofuran was added, presumably to provide a space of the fourth boron atom. However, even this improved yield was too low to make this reaction a promising source of the ferraborane  $B_4H_8Fe(CO)_3$ , which is of particular interest since it is an analogue of  $B_5H_9$  with an  $Fe(CO)_3$  vertex in place of the apical  $BH$  vertex.

The analogy of  $HFe(CO)_3B_3H_8$  to  $HMn(CO)_5$  and  $HCo(CO)_4$  suggested the possibility of the preparation of a nitrosyl derivative  $B_3H_8Fe(CO)_2NO$  analogous to  $Mn(CO)_4NO$  and  $Co(CO)_3NO$ . However, reaction of  $HFe(CO)_3B_3H_8$  with Diazald ( $p-CH_3C_6H_4SO_2N(NO)CH_3$ ) resulted in the

replacement of not only the hydride but also the  $B_3H_8$  ligand with NO groups to give ultimately the well-known<sup>12</sup>  $Fe(CO)_2(NO)_2$  in relatively good yields (~80%). The fate of the boron in this reaction was not determined.

Reactions of  $[R_4N][B_3H_8]$  (R = methyl or n-butyl) were also investigated with a variety of other metal carbonyl halide derivatives including  $C_3F_7Fe(CO)_4I$ ,  $C_5H_5Co(CO)I_2$ ,  $C_5H_5Re(CO)_2Br_2$ ,  $Ir(CO)_3Cl$ ,  $[C_5H_5Mn(CO)_3Cl]^+$ , and  $C_5H_5W(CO)(NO)I_2$ . However, none of these reactions gave any well-defined  $B_3H_8$  or  $B_3H_7$  complexes at least in quantities sufficient for characterization.

Another possible approach for the synthesis of polyhedral boranes involves the coupling of two or three  $B_3H_8$  ligands attached to a single transition metal. In this connection we sought homoleptic derivatives of early transition metals containing two to four  $B_3H_8$  ligands. In attempts to synthesize such derivatives, reactions of  $[R_4N][B_3H_8]$  (R = methyl or n-butyl) were investigated with several early transition metal halides including  $ZrCl_4$ ,  $TaCl_5$ ,  $WCl_4$ , and  $WCl_6$ . The most interesting such reaction was that of  $WCl_6$  with  $[(CH_3)_4N][B_3H_8]$  in diethyl ether or tetrahydrofuran which at  $-78^\circ C$  gave a clear yellow solution. Warming this solution to room temperature, however, led to decomposition of the yellow species to give insoluble dark solids. The stability of this yellow solution was improved by addition of a tertiary amine (e.g., triethylamine or N, N, N', N'-tetramethylethylenediamine) or pyridine but definite products could not even be isolated from the amine-stabilized solutions.

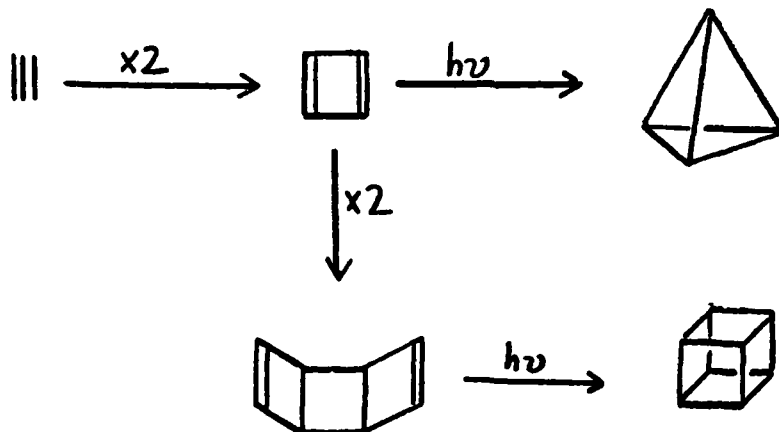
In view of the difficulties in obtaining diverse series of transition metal triborane derivatives from reactions of  $B_3H_8^-$  salts with transition metal halides, we also investigated reactions of various

metal carbonyls with  $C_4H_8O \cdot B_3H_7$  (generated in situ by the reaction of  $B_3H_8^-$  with  $Hg_2Cl_2$  in tetrahydrofuran according to the published procedure<sup>13</sup>). However, attempted reactions of  $C_4H_8O \cdot B_3H_7$  with  $Fe_2(CO)_9$ ,  $Co_2(CO)_8$ ,  $(C_5H_5)_3Ni_3(CO)_2$ ,  $C_5H_5W(CO)_2NO$ , and  $C_4H_8OW(CO)_5$  gave no evidence for the production of stable metal carbonyl triborane derivatives.

For several years the principal investigator (R. B. King) has been interested in the bonding topology of polyhedral boranes, carboranes, and metal clusters.<sup>4</sup> During the course of this research project he extended his theoretical research to the development of simple bonding schemes for eight-vertex  $D_{2d}$  dodecahedral clusters violating Wade's rules.<sup>14</sup> A result from this work is the first rationalization of the different geometries of the two  $D_{2d}$  dodecahedral complexes  $(C_5H_5)_4Co_4B_4H_4$  and  $(C_5H_5)_4Ni_4B_4H_4$ . In the cobalt complex the  $C_5H_5M$  units occupy the vertices of degree 4. Understanding the chemical bonding in polyhedral boranes and carboranes is likely to suggest ultimately new and improved approaches for their synthesis.

## (2) Polyhedrane Synthesis

The following general scheme is of interest for the oligomerization of alkynes to give tetrahedrane and cubane derivatives:



A key to the success of this general scheme is finding the right substituents on the alkyne to promote the necessary chemical reactivity. Also the specific interest of the Army in high energy high density explosives makes of particular interest polyhedranes having substituents which can readily be converted into nitro groups.

In connection with this general scheme Schleyer and co-workers<sup>7</sup> reported in 1978 that the photolysis of dilithium acetylide,  $\text{Li}_2\text{C}_2$ , results in dimerization to give tetralithium tetrahedrane,  $\text{Li}_4\text{C}_4$ . This appeared to be an attractive potential direct route to a variety of substituted tetrahedranes since a priori it seemed that diverse functionalities could be introduced into the tetrahedrane nucleus by reactions of  $\text{Li}_4\text{C}_4$  with appropriate halides or other electrophiles. In this connection we investigated the reaction of the alleged tetralithium tetrahedrane with the halides  $(\text{CH}_3)_3\text{ECl}$  ( $\text{E} = \text{Si}$  and  $\text{Sn}$ ) since the corresponding tetrahedrane,  $[(\text{CH}_3)_3\text{E}]_4\text{C}_4$ , is stable.<sup>8,9</sup>

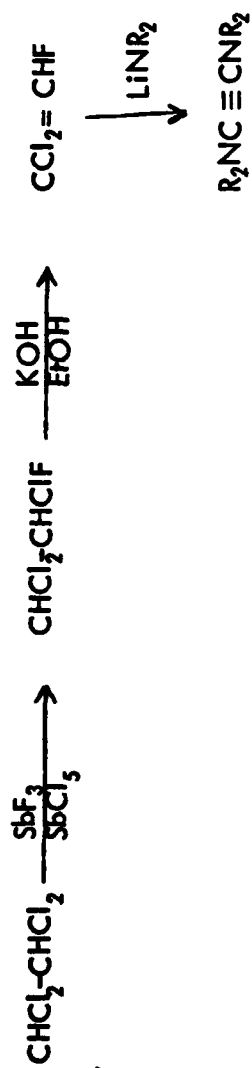
The results of these experiments were quite disappointing. We attempted numerous photolyses of dilithium acetylide in liquid ammonia under conditions similar to those used by Schleyer and co-workers.<sup>7</sup> The liquid ammonia was then removed and an aprotic solvent such as tetrahydrofuran, diethyl ether, hexamethylphosphoramide, or dimethyl sulfoxide was added to the residue. Trimethylchlorosilane or trimethyltin chloride was then added. After stirring at room temperature, attempts were made to isolate any covalent products by conventional methods. However, none of these experiments gave the desired tetrahedrane  $[(\text{CH}_3)_3\text{E}]_4\text{C}_4$  ( $\text{E} = \text{Si}$  or  $\text{Sn}$ ), any conceivable decomposition products thereof, or any other  $[(\text{CH}_3)_3\text{E}]_n\text{C}_n$  polyhedranes. Attempts to photolyze dilithium acetylide in ethereal solvents such as tetrahydrofuran were prevented by the insolubility of dilithium

acetylide in organic solvents in accord with the high stability<sup>15</sup> of solid dilithium acetylide relative to other lithium carbides. We are not sure how to interpret these negative results, but it is clear that the photolysis of dilithium acetylide followed by addition of  $(\text{CH}_3)_3\text{ECl}$  ( $\text{E} = \text{Si}$  or  $\text{Sn}$ ) is not as easy a synthetic route to the substituted tetrahedranes  $[(\text{CH}_3)_3\text{E}]_4\text{C}_4$  as it might have seemed immediately after appearance of the report by Schleyer and co-workers<sup>7</sup> on tetralithium tetrahedrane.

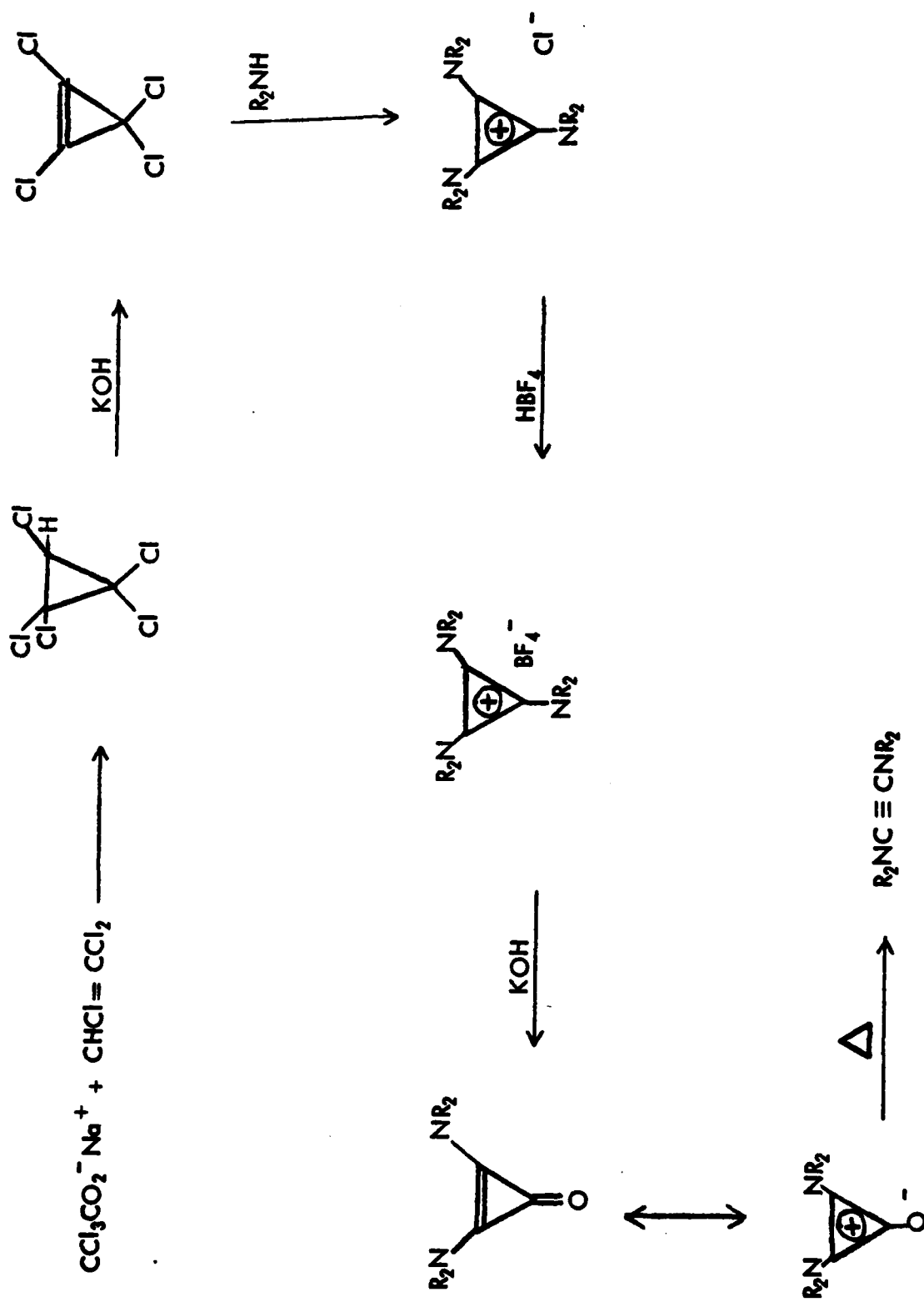
Reaction of methylacetylene with excess n-butyllithium also gives a perlithiocarbon<sup>16</sup>  $\text{Li}_4\text{C}_4$ , which is considerably more soluble in organic solvents than  $\text{Li}_2\text{C}_2$ . However, photolysis of  $\text{Li}_4\text{C}_4$  in tetrahydrofuran solution followed by addition of  $(\text{CH}_3)_3\text{SiCl}$  gave only the persilylated allene  $[(\text{CH}_3)_3\text{Si}]_2\text{C}=\text{C}=\text{C}[\text{Si}(\text{CH}_3)_3]_2$  also obtained when the photolysis step is omitted.<sup>16</sup>

These negative results on the photolysis of lithiocarbons followed by  $(\text{CH}_3)_3\text{ECl}$  addition turned our attention to bis(dialkylamino)acetylenes as a source of per(dialkylamino)polyhedranes. The synthesis of bis(dialkylamino)acetylenes is somewhat of an adventure. Two general schemes are available. Scheme I, developed by Delavarenne and Viehe,<sup>17</sup> uses a nucleophilic reaction of trichloroethylene or preferably 1,1-dichloro-2-fluoroethylene with a lithium dialkylamide followed by dehalogenation. In our hands this method worked for lithium dimethylamide and lithium diethylamide but not for lithium diisopropylamide, lithium pyrrolidide, or lithium piperidide. Scheme II, developed by Wilcox and Breslow,<sup>18</sup> involves decarbonylation of the corresponding bis(dialkylamino)cyclopropenone, which is obtained ultimately from tetrachlorocyclopropene and the corresponding secondary amine. Since





Scheme 1: Bis(dialkylamino)acetylenes via 1,1-dichloro-2-fluoroethylene

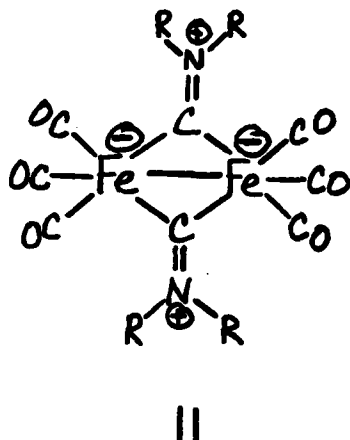


Scheme 2: Bis(dialkylamino)acetylenes via bis(dialkylamino)cyclopropenes

bis(diisopropylamino)cyclopropenone is especially readily available<sup>19</sup> and since the large diisopropylamino substituents on the corresponding acetylene should make this acetylene especially susceptible to oligomerization giving three-dimensional polyhedra rather than two-dimensional polygons, we studied the pyrolysis of bis(diisopropylamino)cyclopropenone at various temperatures using a conventional tube furnace and analyzing the products by gas chromatography-mass spectrometry. Attempted pyrolysis of bis(diisopropylamino)cyclopropenone at 250°C resulted in recovery of unchanged cyclopropenone as the major volatile product. Pyrolysis of the cyclopropenone at 350°C gave some mass spectroscopic evidence for the desired decarbonylation to bis(diisopropylamino)acetylene but the major products did not have  $[(\text{Me}_2\text{CH})_2\text{N}]_n\text{C}_n$  stoichiometries and involved isopropyl fragmentation and migration. Thus the diisopropylamino group does not appear to be thermally robust enough to survive pyrolysis at temperatures sufficient for decarbonylation of bis(diisopropylamino)cyclopropenone.

Since we were unable to pyrolyze bis(diisopropylamino)cyclopropenone to the corresponding acetylene, we investigated other chemistry of this cyclopropenone which might lead ultimately to new per(diisopropylamino)polyhedranes. Photolysis of bis(diisopropylamino)cyclopropenone in either tetrahydrofuran or 1,2-dimethoxyethane gave a low yield of a complex mixture of liquid products: gas chromatography-mass spectrometry indicated that no acetylene or other  $[(\text{Me}_2\text{CH})_2\text{N}]_n\text{C}_n$  products were produced. Reaction of bis(diisopropylamino)cyclopropenone with  $\text{Fe}_2(\text{CO})_9$  in benzene solution gave a 15% yield of  $[(\text{Me}_2\text{CH})_2\text{NC}]_2\text{Fe}_2(\text{CO})_6$  (II: R = isopropyl), an interesting example of an unprecedented removal of a non-carbonyl carbon vertex from a cyclopropenone ring. However,

we did not obtain this complex in sufficient quantities for a detailed study of its chemical reactivity.



In view of these difficulties in obtaining appropriate derivatives of bis(dialkylamino)acetylenes for polyhedrane syntheses, we turned to investigation of the chemistry of the unsymmetrical acetylenes  $(\text{CH}_3)_3\text{SiC}\equiv\text{CNR}_2$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ , and  $(\text{CH}_3)_2\text{CH}$  and  $\text{R}_2\text{N} = \text{piperidino}$ ). These acetylenes are readily obtained from trichloroacetic acid by the following sequence of reactions<sup>20</sup>:

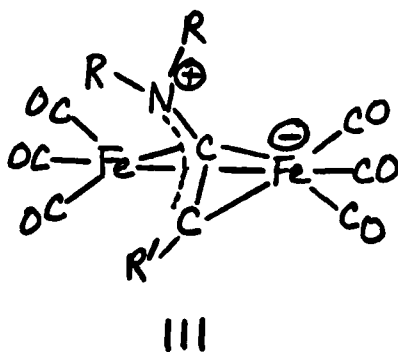
- (1) Conversion of trichloroacetic acid to its acid chloride followed by reaction with a secondary amine to give an amide  $\text{CCl}_3\text{C(O)NR}_2$ .
- (2) Deoxygenation of this amide with a trivalent phosphorus reagent (tri-n-butyl phosphine or triethyl phosphite) to give the trichlorovinyl-amine  $\text{CCl}_2=\text{C(Cl)NR}_2$ .
- (3) Reaction of  $\text{CCl}_2=\text{C(Cl)NR}_2$  with n-butyllithium to give  $\text{LiC}\equiv\text{CNR}_2$  which is quenched by  $(\text{CH}_3)_3\text{SiCl}$  to give  $(\text{CH}_3)_3\text{SiC}\equiv\text{CNR}_2$ .

We investigated the reactions of these acetylenes with metal carbonyls hoping that metal-catalyzed oligomerizations would provide intermediates of potential value for polyhedrane syntheses.

The most extensive studies were done with iron carbonyls. Thus reaction of  $\text{Fe(CO)}_5$  with  $(\text{CH}_3)_3\text{SiC}\equiv\text{CNR}_2$  ( $\text{R}_2\text{N} = \text{diethylamino}$  or

piperidino) in boiling heptane gave mixtures of the yellow cyclobutadiene complex  $[(CH_3)_3Si]_2(R_2N)_2C_4Fe(CO)_3$  and the red tricarbonylferrole-iron tricarbonyl complex  $[(CH_3)_3Si]_2(R_2N)_2C_4Fe_2(CO)_6$ . A structural study by X-ray diffraction on the cyclobutadiene complex ( $R_2N$  = piperidino) in collaboration with Prof. Ray Davis of the University of Texas at Austin indicated it to be the 1,3-isomer I formed by "head-to-tail" dimerization of the unsymmetrical acetylene rather than the 1,2-isomer formed by "head-to-head" dimerization. These products are different from the products obtained from reactions of  $Fe(CO)_5$  with the corresponding symmetrical acetylenes  $(CH_3)_3SiC\equiv CSi(CH_3)_3$  and  $(C_2H_5)_2NC\equiv NC(C_2H_5)_2$  which give the simple acetylene  $\pi$ -complex  $[(CH_3)_3SiC_2Si(CH_3)_3]Fe(CO)_4$ <sup>21</sup> and a mixture of the alkyne dichotomy product  $[(C_2H_5)_2NC]_2Fe_2(CO)_6$  (II:  $R = C_2H_5$ ) and cyclopentadienone complex  $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ ,<sup>22</sup> respectively.

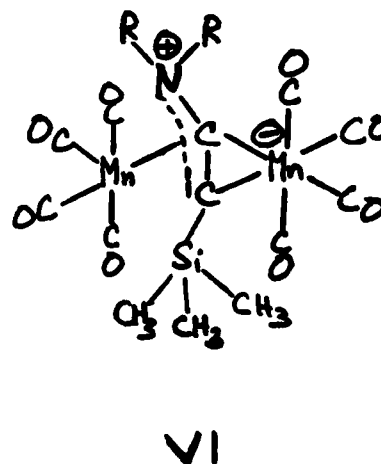
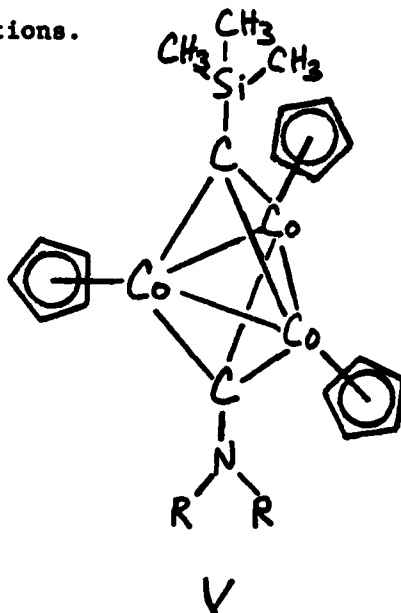
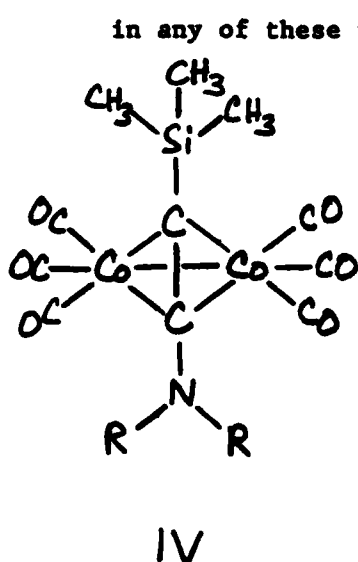
Dimerization of  $(CH_3)_3SiC\equiv CNR_2$  with iron carbonyls is prevented if the reaction is carried out under milder conditions. Thus reactions of  $Fe_2(CO)_9$  with  $(CH_3)_3SiC\equiv CNR_2$  ( $R = C_2H_5$  or  $(CH_3)_2CH$ ) in tetrahydrofuran at room temperature gave red  $[(CH_3)_3SiC_2NR_2]Fe_2(CO)_6$  tentatively formulated as III ( $R' = (CH_3)_3Si$ ) analogous to the reported  $[C_6H_5C_2N-(CH_3)_2]_2Fe_2(CO)_6$  (III:  $R = CH_3$ ,  $R' = C_6H_5$ ).



Some exploratory experiments were performed on the oxidative degradation of the cyclobutadiene complex  $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$  (I: R =  $C_2H_5$ ) in attempts to liberate the free cyclobutadiene or its dimer which would be useful for the synthesis of polyhedranes having equal numbers of dialkylamino and trimethylsilyl pendant groups, both of which could conceivably be converted to nitro groups to give polynitropolyhedranes. However, these experiments appeared to be very unpromising. Thus treatment of  $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$  (I: R =  $C_2H_5$ ) at room temperature with ammonium hexanitratocerate (IV) in ethanol or trimethylamine N-oxide hydrate in acetone or benzene resulted in recovery of most of the iron carbonyl complex. Extended treatment of  $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$  (I: R =  $C_2H_5$ ) at room temperature in acetone solution with ammonium hexanitratocerate (IV) or ferric chloride or reaction of the iron carbonyl complex with anhydrous trimethylamine N-oxide in boiling benzene failed to give any evidence for  $[(CH_3)_3SiC_2N(C_2H_5)_2]_n$  oligomers as indicated by gas chromatography/mass spectrometry analysis of the crude products. We suspect that the bulky  $(CH_3)_3Si$  and  $(C_2H_5)_2N$  substituents in  $[(CH_3)_3Si]_2[(C_2H_5)_2N]_2C_4Fe(CO)_3$  (I: R =  $C_2H_5$ ) shield the iron atom so that more vigorous reagents are needed for oxidative removal of the  $Fe(CO)_3$  group relative to other cyclobutadiene-iron tricarbonyl complexes.<sup>6</sup>

In view of the difficulties outlined above in obtaining intermediates useful for polyhedrane syntheses from reactions of the alkynes  $(CH_3)_3SiC \equiv CNR_2$  with iron carbonyls, reactions of these alkynes with other metal carbonyl derivatives were also investigated. Reactions of the alkynes  $(CH_3)_3SiC \equiv CNR_2$  (R =  $CH_3$ ,  $C_2H_5$ ,  $(CH_3)_2CH$ , or  $R_2N$  = piperidino) with  $Co_2(CO)_8$  in diethyl ether solution at room temperature

gave the corresponding  $[(CH_3)_3SiC_2NR_2]Co_2(CO)_6$  derivatives as dark green solids. Analytical and spectroscopic studies of these complexes suggest formulation as the alkyne-dicobalt hexacarbonyls (IV) although the green colors of these complexes contrast with the dark red colors of known<sup>23</sup> alkyne-dicobalt hexacarbonyls containing exclusively hydrocarbon substituents. Reactions of  $(CH_3)_3SiC\equiv CNR_2$  ( $R = C_2H_5$ ,  $(CH_3)_2CH$ , or  $R_2N =$  piperidino) with  $C_5H_5Co(CO)_2$  in boiling n-octane for 24 hr. gave the corresponding  $[(CH_3)_3SiC_2NR_2]CoC_5H_5$  derivatives as black solids. These derivatives are formulated as the trigonal bipyramidal clusters V analogous to products obtained from reactions of other alkynes with  $C_5H_5Co(CO)_2$ .<sup>22</sup> Ultraviolet irradiation of  $(CH_3)_3SiC\equiv CNR_2$  ( $R_2N =$  diethylamino or piperidino) with  $Mn_2(CO)_{10}$  in tetrahydrofuran solution gave low yields of the corresponding  $[(CH_3)_3SiC_2NR_2]Mn_2(CO)_8$  derivatives as orange solids. Spectroscopic properties of these manganese carbonyl derivatives suggest structure VI. This cobalt and manganese carbonyl chemistry of the alkynes  $(CH_3)_3SiC\equiv CNR_2$  appeared to be of limited value for polyhedrane synthesis since no alkyne oligomerization occurred in any of these reactions.



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PUBLICATIONS AND MEETING PRESENTATIONS ARISING FROM THIS CONTRACT

- (1) R.B. King, L. Borodinsky, and R.M. Murray, "Approaches to the Synthesis of Polyhedranes and Polyhedral Boranes," presented at the Seminar on High Density Energetic Materials, Dover, New Jersey, May, 1982.
- (2) R.B. King and L. Borodinsky, "Octahydrotriborate Transition Metal Complexes as Intermediates in the Syntheses of Boranes and Carboranes," presented at the Working Group Meeting on Boranes, Raleigh, North Carolina, May, 1982.
- (3) R.B. King, "Simple Bonding Schemes for Eight-vertex  $D_{2d}$  Dodecahedral Clusters Violating Wade's Rules," Polyhedron, 1, 133-134 (1982).
- (4) R.B. King and R.M. Murray, "Iron Carbonyl Derivatives as Intemediates in Polyhedrane Synthesis," paper presented at the Working Group Meeting on Synthesis of High Density Energetic Materials, Dover, New Jersey, April, 1983.
- (5) R.M. Murray, R.B. King, R.E. Davis, and P.K. Ross, "Metal Carbonyl Chemistry of Dialkylaminotrimethylsilylacetylenes," presented at the XI International Conference on Organometallic Chemistry, Callaway Gardens, Georgia: abstracts, p.110.
- (6) R.B. King, R.E. Davis, R.M. Murray, and P.K. Ross, "Metal Carbonyl Derivatives of Dialkylaminotrimethylsilylacetylenes: Crystal and Molecular Structure of a Cyclobutadiene-iron Tricarbonyl Complex formed by Head-to-tail Dimerization of a Dialkylaminotrimethylsilylacetylene," to be written up for publication as soon as the complete crystallographic data are received from Prof. R.E. Davis.

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